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Electronic Properties and Orbital-Filling Mechanism in Rb-Intercalated Copper Phthalocyanine

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The evolution of the electronic properties of a thin film of copper phthalocyanine deposited on Al(100) and progressively intercalated with rubidium atoms was followed by photoemission and X-ray absorption spectroscopies. Electron donation from the Rb atoms to the $C_{32}H_{16}N_8Cu$ molecules results in the lifting of the degeneracy in the e_g ligand-derived molecular orbital and the lowering of the molecular symmetry. For $Rb_{\sim 2}C_{32}H_{16}N_8Cu$, spectral evidence indicates that both donated electrons reside in the first split-off e_g -derived level, thus creating an electronic inequivalence between the C atoms in the benzene rings. For higher Rb concentrations, a reduction of the Cu oxidation state is observed, together with a new Cu-derived state in valence-band photoemission spectra, testifying to the filling of the b_{1g} orbital. Thus, even though b_{1g} is the lowest unoccupied orbital of the neutral molecule, in the film, the Cu-derived b_{1g} -derived states are occupied only after a partial filling of the e_g -derived band has taken place. Despite the fact that the e_g -derived spectral weight becomes larger as the rubidium content in the $Rb_xC_{32}H_{16}N_8Cu$ compound increases, no spectral density was observed at the Fermi level, showing that the film remains insulating for all of the investigated stoichiometries.

I. Introduction

The control of charge carriers in an organic matrix represents both a great challenge in view of technological applications involving organic-semiconductor-based devices and a means to expand our understanding of electron transport in organic crystals. The latter are typically semiconducting molecular crystals in which the molecules interact via weak van der Waals forces and the electronic structure of the crystal strongly resembles that of the isolated molecule.^{1,2} The weak overlap between wave functions associated with neighboring molecules also implies that the electron–electron Coulomb interaction U is large compared to the kinetic energy of the electrons involved in conduction. This means that, when charge is transferred into the lowest unoccupied molecular orbital (LUMO) to achieve partial filling, these materials can behave as Mott insulators instead of showing metallic behavior.³

The easiest and most effective way to achieve charge transfer to an organic semiconductor is intercalation with alkali metal atoms. The best-known examples of how new electronic phases can be created in this manner are C_{60} -based crystals. For buckminsterfullerene, the LUMO is triply degenerate because of the high symmetry of the molecule and can therefore host up to six electrons. Upon intercalation, metallic and superconducting phases, as well as Mott–Hubbard insulators, are observed, depending on the particular stoichiometry of the alkali

fulleride.^{4–7} However, a recent theoretical study⁸ predicts that such a rich scenario of electronic phases is not limited to fullerides but can also be achieved for other high-symmetry conjugated planar molecules such as phthalocyanines. Most metal phthalocyanines (MPC's) are characterized by a doubly degenerate LUMO,⁹ with copper phthalocyanine ($C_{32}H_{16}N_8Cu$, called CuPc in the following) also having a half-filled b_{1g} 3d-derived electronic level located between the highest doubly occupied ligand orbital a_{1u} and the LUMO; in other MPC's such as zinc phthalocyanine, the b_{1g} orbital is lower in energy and completely filled, and the a_{1u} orbital is the highest occupied molecular orbital (HOMO). The metallicity of alkali-intercalated phthalocyanine films is still a controversial issue: Whereas transport measurements¹⁰ clearly demonstrate the formation of a metallic state upon K-intercalation of transition-metal phthalocyanine films and the return to insulating behavior when the potassium content exceeds a critical value, photoemission studies do not identify any stoichiometry characterized by a spectral density at the Fermi level,^{11,12} and electron energy loss spectra collected in transmission¹³ reveal no closing of the gap upon progressive alkali intercalation.

To better understand this issue, we decided to study the nature of the bonding between an alkali metal (Rb) and the organic molecule CuPc and to investigate how the charge transfer occurs. We chose Al(100) as the substrate because it represents a very particular template for CuPc growth; in fact, from the second layer onward, the molecules assume a quasi-standing orientation,^{14,15} rather different from the better-known α and β phases obtained on other substrates.^{16–19} Through photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) measurements, we are able to identify the orbitals that host the

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charge donated by Rb, and by comparing the chemical shifts of the C 1s core level for both benzene and the pyrrole carbon with progressive Rb intercalation, as well as those for N 1s and Cu 2p_{3/2}, we can deduce where the Rb ions are located.

II. Experiment

All measurements were performed at the Elettra synchrotron in Trieste, Italy, at the BEAR bending magnet beamline,²⁰ which is equipped with a grazing-incidence monochromatizing section based on a plane grating–plane mirror design, delivering a spot size 300 $\mu\text{m} \times 30 \mu\text{m}$, and a UHV system with a preparation and a spectrometer chamber, the latter housing a hemispherical analyzer. The C 1s and Rb 3d core-level photoemission spectra were collected with $h\nu = 380 \text{ eV}$ and a total energy resolution of 300 meV; those of the N 1s (Cu 2p_{3/2}) region were measured with $h\nu = 500 \text{ eV}$ ($h\nu = 1070 \text{ eV}$) and a total energy resolution of 500 meV, whereas the valence-band photoemission spectra were collected with $h\nu = 20 \text{ eV}$ with a total energy resolution of 200 meV. All core-level spectra were referenced to the tabulated binding energy (BE) of the Al 2p_{3/2} core level of 72.70 eV,²¹ whereas the valence-band spectra were referenced to the Fermi level of the clean Al substrate. X-ray absorption spectra were collected in drain-current mode in a geometry for which the incidence angle was kept fixed at the value of 10°; for both the carbon and nitrogen K edges, the photon energy resolution was 150 meV.

The Al(100) surface was cleaned by sputtering ($E_{\text{Ar}^+} = 3 \text{ keV}$) and annealing ($T = 680 \text{ K}$), and the cleanliness was checked by photoemission analysis of the Al 2p core level. Commercial C₃₂H₁₆N₈Cu (Sigma-Aldrich, 99% purity, used as received) was sublimed from a quartz crucible at a pressure of $\sim 10^{-9}$ mbar. The deposition rate, measured with a quartz microbalance placed in the same position as the sample, was 2 Å/min, which, for a deposition time of 25 min, gives a nominal thickness of the pristine CuPc film of 50 Å. Rb was dosed from a well-outgassed SAES Getter dispenser. The Rb concentration in the organic matrix was evaluated from the intensity ratio of the C 1s and Rb 3d core-level photoemission signals corrected for the different photon cross sections, the different mean free paths (8 and 14 Å for photoelectrons coming from C 1s and Rb 3d, respectively, calculated with the program available at www.lasurface.com, which uses the modeling functions of the inelastic mean free path from refs 22 and 23), and the stoichiometry of CuPc. In this energy region, the throughput of the analyzer does not change significantly²⁰ and was therefore not included in the calculation of the Rb concentration. Nominal stoichiometries of Rb_xC₃₂H₁₆N₈Cu obtained this way are indicated as Rb_xCuPc throughout this article and represent the average composition of our samples within the probing depth of PES. Based on our sporadic tests of the uniformity of Rb intercalation in various points of the sample, we believe that 0.2–0.3 can be considered a reasonable estimate of the error bar on x , thus giving a very large error for the lowest stoichiometries (up to 100%) that becomes progressively less significant with increasing Rb concentration.

III. Results

Cu 2p_{3/2} Core-Level Photoemission Spectra. In Figure 1, the evolution of Cu 2p_{3/2} photoemission line is displayed as a function of the alkali content of the copper phthalocyanine film. Pristine CuPc, also reported for comparison, shows a single peak at a BE of 935 eV, as previously reported and assigned to Cu(II). Upon the creation of a hole in the 2p level, two final electronic configurations are possible: the photoemission line

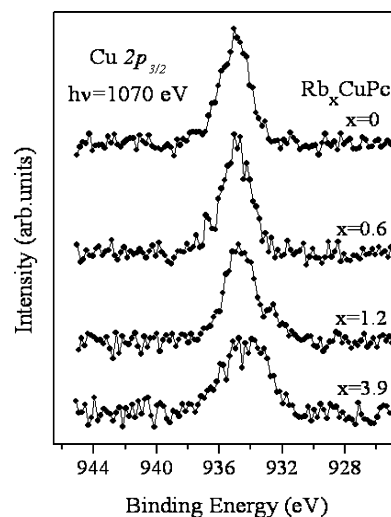


Figure 1. Photoemission spectra of the Cu 2p_{3/2} core-level region of a thin copper phthalocyanine film intercalated with rubidium as a function of Rb concentration.

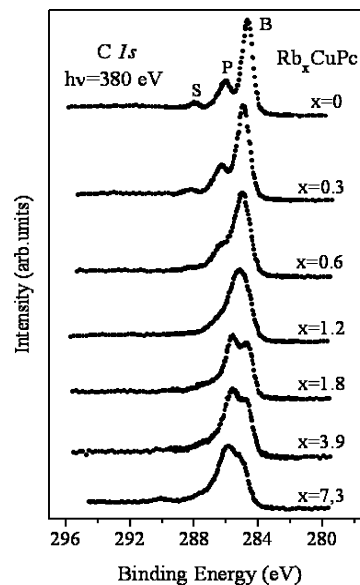


Figure 2. Photoemission spectra of the C 1s core-level region of a thin copper phthalocyanine film intercalated with rubidium as a function of Rb concentration. Labels on the pristine spectrum account for emission from benzene rings (B), emission from pyrrole rings (P), and a shakeup satellite (S).

corresponding to 2p⁵3d⁹ appears at higher BE than that in which the hole in the 3d level is screened by the ligand of the molecule (2p⁵3d¹⁰L⁻¹ configuration).^{24–26} In phthalocyanine complexes, the latter exhibits a larger intensity and for this reason is usually called as the main Cu 2p line.²⁴

Progressive intercalation of the molecular film does not lead to a shift of the Cu(II) component but gives rise to a new feature at lower BE, first visible as a shoulder for Rb_{1.2}CuPc and then becoming as high as the Cu(II) component at the highest rubidium concentration (Rb_{3.9}CuPc). This extra peak at a BE of approximately 933.5 eV is typical of both Cu(I) and Cu(0),²⁷ and thus indicative of charge transfer from Rb to CuPc.

C 1s Core-Level Photoemission Spectra. In Figure 2, a selection of C 1s core-level photoemission spectra taken at different rubidium concentrations is displayed. For pristine CuPc, a three-peak-shaped structure is visible, where the peaks labeled as B and P account for carbon contributions from benzene and pyrrole rings, respectively. Peak S is usually

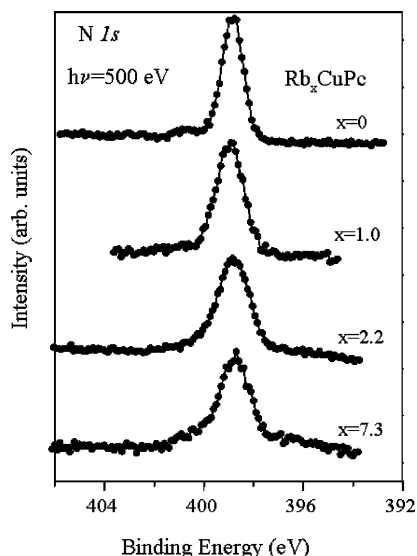


Figure 3. Photoemission spectra of the N 1s core-level region of a thin copper phthalocyanine film intercalated with rubidium as a function of Rb concentration.

assigned to a shakeup satellite²⁴ where the creation of a hole in the C 1s level is accompanied by the promotion of an electron from the HOMO to the LUMO. Indeed, the energy distance between S and P is very close to the optical energy gap (about 1.8–1.9 eV, as also measured by energy loss spectroscopy¹⁴). The equivalent shakeup satellite associated with the benzene rings is hidden under peak P.

As the molecular matrix is progressively intercalated, the line shape changes dramatically. The first change is a shift toward higher BE without any significant effect on the line shape (Rb_{0.3}CuPc); then, for Rb_{0.6}CuPc, the valleys between B and P and between P and S decrease as a consequence of a general spectral broadening. For Rb_{1.2}CuPc, a single larger peak dominates the spectral density. Its asymmetry toward higher binding energies can be interpreted as a trace of peak P, whereas the satellite peak S is no longer detectable. For Rb_{1.8}CuPc, a new component at 285.55 eV is evident, whereas the B-derived peak remains at 284.75 eV. Upon further doubling the Rb content no significant changes occur: the two peaks are less well resolved, but remain clearly distinguishable. For Rb_{7.3}CuPc, the spectrum is shifted toward higher BE, with the two major components being more extensively merged, and an additional feature appears peaked at a BE of 290.10 eV. The latter proved to be extremely sensitive to the synchrotron light and disappeared after prolonged irradiation, indicating that it is probably due to the outermost CuPc layer.

N 1s Core-Level Photoemission Spectra. Figure 3 shows the evolution of the N 1s photoemission line shape as a function of the Rb concentration in the Rb_xCuPc film. The pristine spectrum is characterized by a main component located at a BE of 398.9 eV, accounting for both the N atoms connected to the center of the molecule and the atoms bridging the isoindolic units. The small peak at a BE of 400.75 eV comes from a shakeup satellite, similar to that seen in the C 1s PES.²⁴ The spectral changes induced by alkali intercalation are quite small compared to those observed for the C 1s and Cu 2p_{3/2} photoemission lines: For Rb_{1.0}CuPc, a 0.15 eV shift toward higher BE can be detected, together with a slight broadening; for Rb_{2.2}CuPc, the full width at half-maximum (fwhm) increases by ~15%, without any changes occurring in the general line

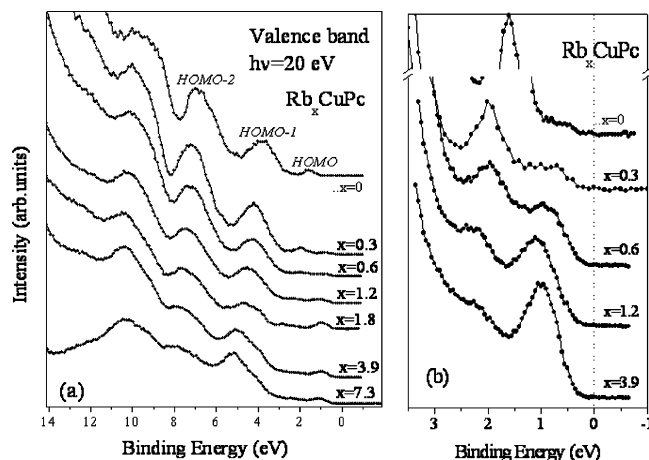


Figure 4. (a) Valence-band photoemission spectra collected at $h\nu = 20$ eV of a thin copper phthalocyanine film intercalated with rubidium as a function of Rb concentration. The molecular-orbital-derived structures in the pristine spectrum are labeled according to common literature convention. (b) Enlargement of the energy region close to the Fermi edge (dashed line).

shape. For the highest Rb concentration (Rb_{7.3}CuPc), the fwhm shrinks again, and the centroid shifts 0.20 eV back to lower BE.

Valence-Band Photoemission Spectra. The valence-band evolution of the Rb-doped copper phthalocyanine system is presented in Figure 4a. Starting from the pristine CuPc spectrum, we focus our attention on the three main features, namely, the a_{1u} -derived feature (corresponding to the HOMO in other MPc's such as ZnPc) at 1.54 eV and other two structures located at 3.8 and 6.9 eV that we call HOMO - 1 and HOMO - 2, respectively, in accordance with common literature convention. As for the core-level spectra, the first effect of alkali intercalation is a shift toward higher BE (0.25 eV) accompanied by minor changes in line shape. For Rb_{0.6}CuPc, the spectral density seems not to shift any further, but the three main features appear broader and less intense. In particular, as better highlighted in the enlargement displayed in Figure 4b, the a_{1u} -derived band broadens significantly with increasing alkali concentration, and a new feature appears closer to the Fermi level. Because this feature grows in intensity as the Rb content increases, we assign it to the progressively filled LUMO-derived band. For Rb_{1.8}CuPc, the Rb concentration for which C 1s shows the doublet for the first time, no new spectral features are observed, but the LUMO-derived band is now a well-defined peak. For Rb_{3.9}CuPc, for which two different Cu oxidation states can be detected in the Cu 2p_{3/2} photoemission spectrum, the (HOMO - 1)-derived feature shows a different line shape because of a new structure arising at a BE of about 5 eV. This is even more evident when we move to Rb_{7.3}CuPc, where the extra feature is clearly superimposed on the (HOMO - 1)-derived spectral intensity. Focusing on Figure 4b, it is possible to see the LUMO-derived peak progressively increasing with Rb content, though never giving rise to any spectral density at the Fermi level.

C K-Edge Absorption Spectra. In Figure 5, we report the C K-edge absorption spectra collected for a copper phthalocyanine film progressively intercalated with Rb. The spectrum corresponding to the pristine CuPc film is characterized by three main structures located at 285.8, 287.8, and 289.7 eV, assigned to transitions from the C 1s core level to the LUMO-, (LUMO + 1)-, and (LUMO + 2)-derived bands, respectively.² The first peak clearly shows a shoulder (marked B) at about 285.3 eV related to the 24 benzene C atoms and a more intense component at 286.0 eV involving the 8 C atoms residing in the pyrrole

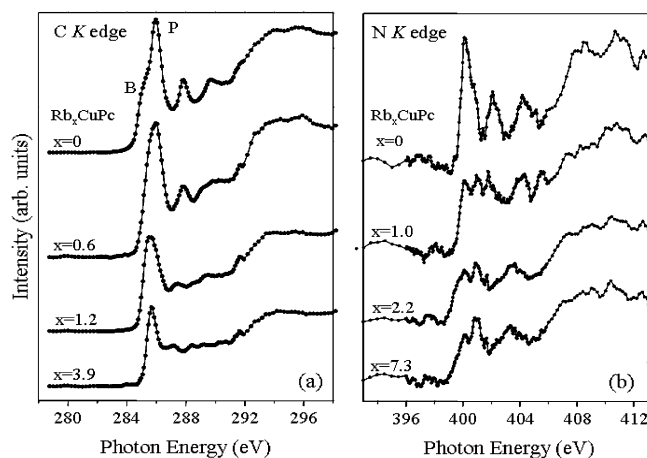


Figure 5. (a) C 1s and (b) N 1s NEXAFS spectra of a thin copper phthalocyanine film intercalated with rubidium as a function of Rb concentration.

rings. The relative intensity of the shoulder compared to the main component does not follow the stoichiometric ratio between the two types of carbon because of the strong localization of the LUMO orbital in the pyrrole rings.² Upon alkali intercalation, peak P, due to pyrrole carbons, progressively loses intensity and shifts to 285.7 eV, thus removing the effect of a two-fold feature for the LUMO-derived peak. The other structures are rigidly shifted toward lower photon energy; in particular, the second main feature moves from 287.8 to 287.4 eV. For $\text{Rb}_{3.9}\text{CuPc}$, the spectrum seems more structured, but it is hard to assign the new features to specific unoccupied states because a theoretical study of the electronic structure of this system is not available.

N K-Edge Absorption Spectra. Absorption measurements at the N K edge are reported in right panel of Figure 5 for pristine CuPc and various Rb-intercalated films. These spectra are much noisier than those collected at the C K edge, first because the C/N stoichiometric ratio in phthalocyanines is 4:1, and second because the photon flux at the BEAR beamline, at around 400 eV, is half that at the C K edge. The spectrum of pristine CuPc shows three main features similar to those for the C K edge that stem from transitions from the N 1s orbital to the LUMO, LUMO + 1, and LUMO + 2. It is particularly interesting to point out the different shape exhibited by the feature at a BE of about 400.4 eV. Whereas in the case of the C K edge a two-fold structure is evident, here, the smaller inequivalence experienced by nitrogen atoms results only in a shoulder at higher $h\nu$. As soon as Rb is added to the organic matrix, the first main feature strongly decreases in intensity and shifts to lower energy. The other features also seem to shift, although no definite conclusion can be drawn on this point because of the poor statistics.

IV. Discussion

The first aspect to discuss is the metallicity of the film. Figure 4a,b clearly shows that Rb-doped copper phthalocyanine films do not become metallic. In fact, even though the LUMO-derived band is progressively filled, no spectral density can be detected at the Fermi level. By comparing the PES binding energies of the C 1s and N 1s core levels in Figures 2 and 3 with the onset of adsorption at the C and N K edges, one can also obtain information about the metallic screening present in the system. In fact, in the case of a metal-like screened core hole, in which the screening electron comes from the Fermi level, the core-ionized final state corresponds to the lowest X-ray absorption

final state.²⁸ For a truly metallic system such as C_{60} chemisorbed on a metal substrate, this implies that the C 1s binding energy coincides with the center of the C 1s \rightarrow LUMO absorption feature in the NEXAFS spectrum.²⁹ This is clearly not the case for the samples studied here: For instance, for $\text{Rb}_{3.9}\text{CuPc}$, the C 1s centroid in the photoemission spectrum is at a BE of about 285.6 eV, whereas the single peak in the C K edge appears at 285.75 eV. Similarly, for $\text{Rb}_{7.3}\text{CuPc}$, the N 1s line appears at a BE of 398.75 eV, whereas the N K edge has a first peak at a photon energy of 400.1 eV. The absence of spectral density at the Fermi level for all Rb_xCuPc compounds is in agreement with the results of two previous photoemission experiments on phthalocyanines,^{11,12} but as already mentioned in the Introduction, it contradicts the transport measurements of Craciun and co-workers,¹⁰ who found metallic behavior for K-intercalated transition-metal phthalocyanines. One reason for this discrepancy could be the different probing depths of these experimental techniques: In the case of photoemission experiments, the probed portion of the sample is limited by the mean free path, which, for the experimental conditions considered in this work, never exceeded 16 Å.^{22,23} In contrast, a transport measurement is not surface-sensitive, because the signal is gathered from the entire sample. It would thus be tempting to conclude that only the bulk region of the alkali-intercalated organic compound becomes metallic. However, a recent investigation using bulk-sensitive electron energy loss spectroscopy in transmission on K-intercalated CuPc revealed no metallicity,¹³ thus implying that some other mechanism at the origin of metallicity is not being taken into account. A possibility to be considered is the packing of CuPc molecules in the film grown on Al(100), which, as already mentioned, is different^{14,15} from that of the films grown on Si(001)-1 \times 2 used in the transport measurements. Differences in the molecule–molecule distance and orientation lead to different overlaps of the π orbitals and hence to different electron correlation properties.⁸ Theoretical calculations might help to clarify whether this is the reason for the lack of metallicity in our films.

We now focus on the orbital-filling mechanism in copper phthalocyanine. The very first effect of alkali deposition is a change in the work function evidenced by the shift of the energies in both the core-level and valence-band spectra without any change in the line shapes. The first band to accept charge donated from the alkali atoms is the C-derived LUMO: The C 1s line (Figure 2) shows striking changes, whereas the Cu $2p_{3/2}$ spectrum (Figure 1) is still unaffected. While the electronic structure of the isolated neutral molecule⁹ would suggest that the orbital-filling order involves first the b_{1g} orbital and then the LUMO, our spectroscopic evidence suggests the opposite. This is probably due to a higher Coulomb repulsion in the strongly localized b_{1g} orbital than in the more delocalized e_g ligand-derived orbital, in agreement with photoemission data from the isolated molecule,² which indicated that the ionization energy of the ligand-derived a_{1u} orbital is lower than that of the Cu-derived b_{1g} orbital. Such a scenario was also described by Liao and Scheiner⁹ and very recently confirmed by theoretical predictions³⁰ according to which the addition of extra charges results in the filling of the e_g (the LUMO) orbital rather than the b_{1g} (Cu-derived) orbital even for two and three extra electrons.

A further issue to consider is the hypothesis, first advanced by Giovanelli et al.¹² for $\text{K}_x\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$ and then confirmed by Flatz et al.¹³ in the case of K_xCuPc , that two distinct phases are formed: K_2CuPc and K_4CuPc . If we focus on the evolution of the C 1s core-level photoemission spectrum with increasing Rb

content of the film (see Figure 2) and trace a vertical line starting from the centroid of the B peak in the $\text{Rb}_{0.3}\text{CuPc}$ spectrum, we observe that the B peak seems not to disperse any more after the initial shift, whereas a new component at a BE of 285.55 eV rises. The presence of the new component together with the pristine B component might suggest the coexistence of two phases with different stoichiometries. In particular, as the doublet appears for a Rb concentration close to 2 ($\text{Rb}_{1.8}\text{CuPc}$), one could argue that the peak at 284.75 eV deriving from the B peak in the pristine CuPc accounts for pristine molecules, whereas the peak at 285.55 eV stems from Rb_2CuPc molecules. Giovanelli et al.,¹² who observed essentially the same spectrum for $\text{K}_{3.9}\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$ as we do for $\text{Rb}_{3.9}\text{CuPc}$, claimed that the two main peaks correspond to the benzene-derived contributions of the two stoichiometries $\text{K}_2\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$ and $\text{K}_4\text{C}_{32}\text{H}_{16}\text{N}_8\text{Zn}$. Nonetheless more than one piece of spectroscopic evidence leads us to think that this is not the case. The first evidence comes from the evolution of the N 1s photoemission spectrum: In this case, very small changes occur in both the line shape and the energy position, whereas a doublet structure or a larger line width would be expected for two phases. In addition, our efforts to reconstruct the valence-band spectra of $\text{Rb}_{1.8}\text{CuPc}$ and $\text{Rb}_{3.9}\text{CuPc}$ (Figure 4) as the superposition of two different spectra (each coming from a different stoichiometry) were unsuccessful, thus making the hypothesis of phase separation unlikely. However, most importantly, the C K-edge absorption spectrum of $\text{Rb}_{3.9}\text{CuPc}$ (corresponding to a Rb concentration for which the C 1s doublet is very well resolved in the photoemission spectrum) shows an extremely narrow feature, not compatible with a superposition of two phases, which, on the contrary, should give rise to features larger than those of pristine CuPc. Consequently, we believe that the doublet observed in the evolution of the C 1s spectrum as a function of Rb intercalation is due not to the coexistence of two phases, but to a single phase, the details of which are elucidated in the remainder of this section.

As already discussed, the C 1s doublet is best resolved for $\text{Rb}_{1.8}\text{CuPc}$. Our hypothesis is that the two extra electrons from the Rb atoms together populate one of the initially degenerate LUMO-derived bands. This degeneracy is lifted as soon as alkali intercalation takes place, so that the second extra electron arriving will fill the already half-filled LUMO-derived band rather than filling the lifted second LUMO-derived band. This was also claimed by Flatz et al.¹³ for K_xCuPc . The LUMO spatial distribution exhibits D_{4h} symmetry as a result of the sum of the two energy-degenerate molecular orbitals. Once an extra charge is introduced, the degeneracy is lifted, and the symmetry passes from D_{4h} to D_{2h} . Calculations on the free CuPc molecule² indicate that the two resulting LUMOs (say, LUMO' and LUMO'') exhibit two spatial distributions that are equal but rotated by 90° with respect to each other. If LUMO' is filled and LUMO'' is empty, the C atoms in two adjacent benzene rings will no longer be equivalent because the benzene rings residing in the part of the molecule where LUMO' is filled will experience a different electronic environment. Alkali ions were recently predicted³⁰ to sit above the center of a phenyl ring in the case of K_2CuPc , thus further marking the difference between the two possible benzene rings. All of this will result in two different binding energies, as we observe experimentally. Such a picture would also explain why only minor effects are detected in the N 1s core-level spectra (Figure 3). In fact, the N atoms are all close to the central part of the molecule, so that no matter which LUMO is filled, they will always be affected in similar ways. The reason why no significant binding energy shift

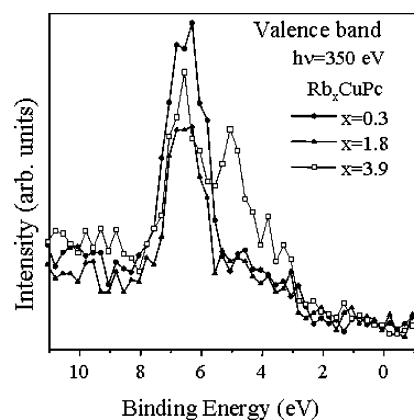


Figure 6. Selection of valence-band photoemission spectra of a thin copper phthalocyanine film intercalated with rubidium, collected at $h\nu = 350$ eV, as a function of Rb concentration.

(significant compared to the C 1s case) is detected might be because the shift to high BE induced by the upshift of the Fermi level is compensated by the screening effect induced by extra charge coming from the alkali atoms. The localization of charge, due to LUMO filling, in the central part of the molecule is also supported by the N K-edge NEXAFS spectra (see Figure 5b), in which the LUMO-derived features are already quenched for the first Rb depositions.

We now discuss intercalation beyond Rb_2CuPc . The reason for the minimal change in the C 1s core-level spectrum on moving from $\text{Rb}_{1.8}\text{CuPc}$ to $\text{Rb}_{3.9}\text{CuPc}$ is that, before filling the second LUMO level (LUMO''), electrons tend to fill the b_{1g} Cu-derived level first. This is verified by the evolution of the Cu $2p_{3/2}$ line shape (Figure 1), which shows the reduction of the copper oxidation state from Cu(II) to Cu(I) as a consequence of the b_{1g} orbital becoming filled. Further evidence comes from changes in the valence-band spectra where the extra peak at the BE of about 5 eV appears exactly when the reduction of copper atoms takes place. To support this claim, Figure 6 shows the valence-band spectra collected at a photon energy of 370 eV for $\text{Rb}_{0.6}\text{CuPc}$, $\text{Rb}_{1.8}\text{CuPc}$, and $\text{Rb}_{3.9}\text{CuPc}$. These three concentrations of Rb are representative of three different steps in Rb intercalation: a first step in which no major change in the C 1s line shape has occurred, a second step in which the C 1s doublet is best resolved, and a third step in which Cu reduction has taken place. As the photon energy is changed from 20 to 370 eV, the relative cross sections of C-derived and Cu-derived orbitals in the valence band change dramatically. More specifically, at 370 eV, the Cu-derived orbitals exhibit a much higher cross section than the ligand-derived orbitals. In Figure 6, for the lower Rb concentrations, only one peak is visible, which is a Cu 3d-derived orbital.² The fact that $\text{Rb}_{1.8}\text{CuPc}$ also shows a single peak confirms that the first donated electrons populate the LUMO, thus not affecting the half-filled b_{1g} Cu-derived orbital. For $\text{Rb}_{3.9}\text{CuPc}$, a new peak appears at the same BE as the extra peak in Figure 4. Given the Cu reduction visible for the same sample in the Cu $2p_{3/2}$ spectrum (Figure 1), we can claim that the peak centered at a BE of ~5 eV has to be ascribed to Cu having changed its oxidation state. This order of orbital filling also agrees with the C K-edge NEXAFS spectrum for $\text{Rb}_{3.9}\text{CuPc}$, which includes a very narrow feature corresponding to the still partially empty second LUMO (LUMO''). In fact, if the four electrons were all transferred to the two LUMO-derived bands, the first C $1s \rightarrow \pi^*$ transition would no longer be observable.

The last point to discuss is the possibility that Rb atoms replace Cu atoms in the center of the phthalocyanine molecule.

In fact, it was recently observed that, in the case of heavily potassium-doped CuPc prepared by cosublimation, $C_{32}H_{16}N_8K$ complexes can be obtained.³¹ Additionally, the authors of ref 31 detected diffraction due to the face-centered-cubic unit cell of elemental Cu, which provided the signature of its formation as a product of the reaction between CuPc and potassium and which implies that Cu should be present as metallic clusters.

Indeed, the two peaks that we observe in the Cu $2p_{3/2}$ core-level spectrum for $Rb_{3.9}CuPc$ would be compatible with this hypothesis because the BE of metallic Cu is approximately the same as the BE of Cu in its monovalent state.²⁷ Likewise, the extra feature observed in the valence-band spectrum could be thought to derive from copper clusters formed after the replacement of Cu by Rb at the center of the phthalocyanine. However, if metallic copper were formed, one should observe the Cu 3d levels at the characteristic BE position of metallic Cu (exhibiting a band centered at a BE of ~ 2.5 eV; see ref 32) and not at 5 eV (see Figure 6). Moreover, if Cu replacement had taken place, both the electronic structure of the outer molecular orbitals and the nitrogen environment (N atoms are linked to the central metal atom) would have been deeply influenced. This is not the case, and even for $Rb_{7.3}CuPc$, the N 1s core-level spectrum shows only a slight energy shift (see Figure 3). As a consequence, we believe that, for the phases studied in this work, Cu replacement does not take place (although no definite proof can be provided).

IV. Conclusions

Our study of the changes in electronic structure of a copper phthalocyanine thin film as a function of stepwise Rb intercalation found that, although the Cu-derived b_{1g} orbital lies lower in the energy level diagram of the neutral molecule, it is occupied in the molecular solid only after partial filling of the e_g ligand-derived molecular orbital has taken place. We ascribe this behavior to a larger Coulomb repulsion in the strongly localized Cu-derived orbital. In particular, electron donation results in a lifting of the degeneracy of the e_g -derived band and a lowering of the molecular symmetry. For $Rb_{\sim 2}CuPc$, spectral evidence indicates that both electrons reside in the first split-off e_g -derived level, thus rendering the C atoms in the benzene rings no longer all equivalent. For higher Rb concentrations, some of the Cu atoms assume a lower oxidation state, and a new Cu-derived state appears in the valence-band spectra, thus testifying to the filling of the b_{1g} orbital. In the films investigated, no trace of spectral density at the Fermi level was found at any stage of rubidium intercalation. This might be a consequence of different molecule–molecule distances and orientations in our films grown on Al(100) compared to those in films grown on Si (100)- 2×1 , for which metallicity induced by alkali intercalation was found by scanning tunneling spectroscopy and transport measurements.¹⁰ Theoretical calculations on correlation effects considering the molecular packing of CuPc on Al(100) could resolve this question.

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